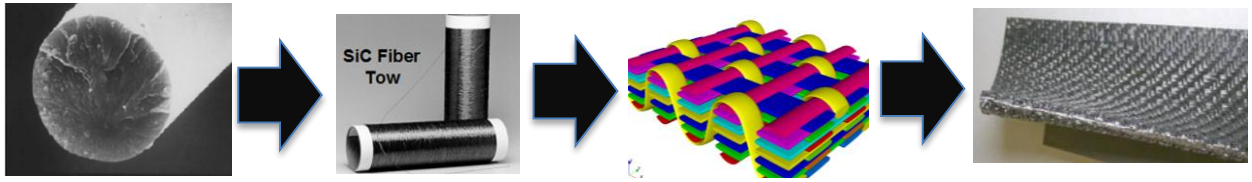
Ultra High Temperature (UHT) SiC Fiber

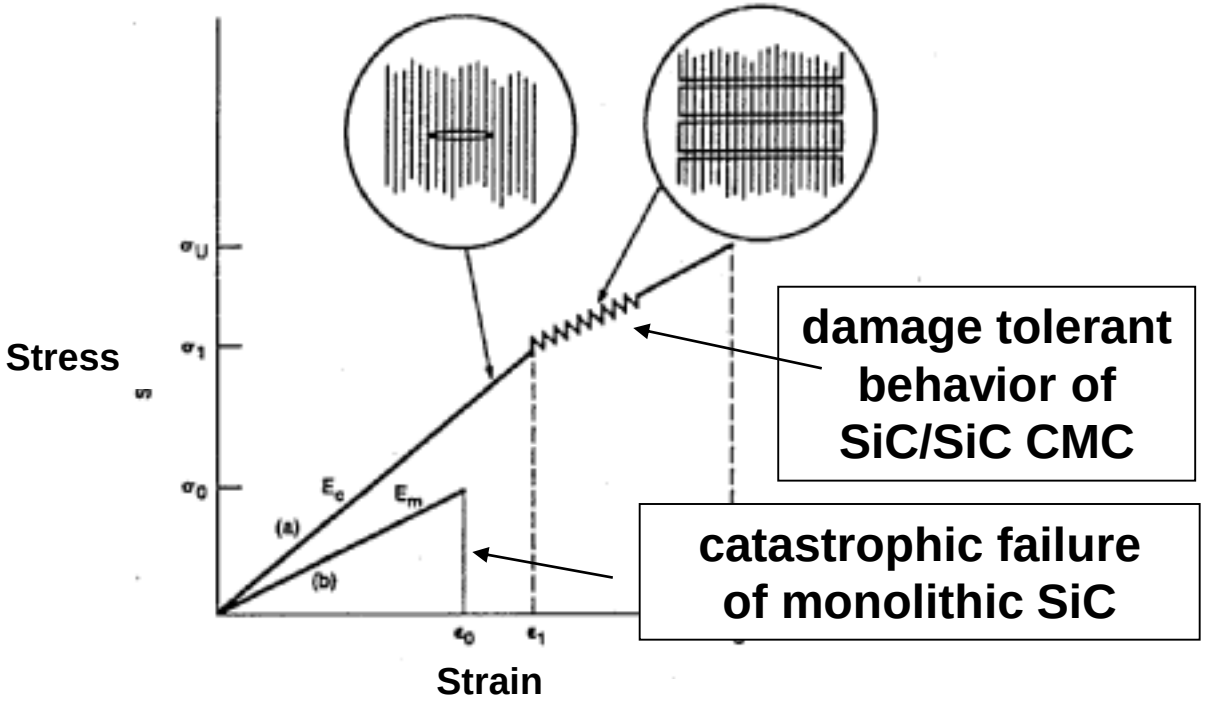
Presentation to NASA Aeronautics Research Institute at Completion of a Phase 2 Seedling Fund Task
(03/18/2015)

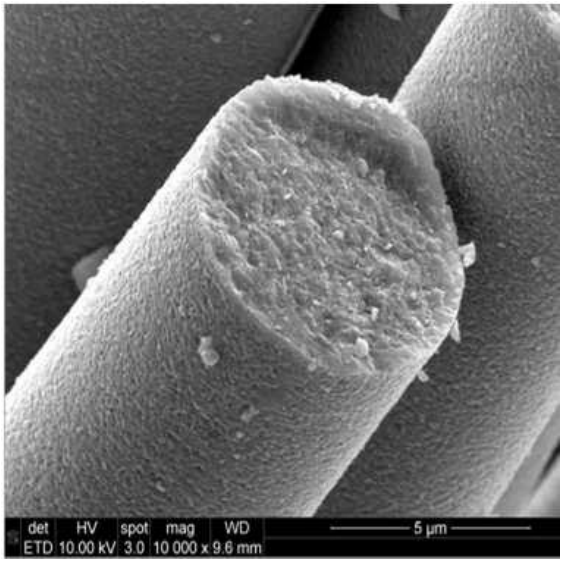


NASA Glenn Fiber Team and Expertise:

Dr. J. DiCarlo (PI) – Fiber Theory and Experimental Experience
Dr. N. Jacobson – High Temperature Chemistry
Dr. M. Lizcano – Material Science, Fiber Processing
Dr. R. Bhatt (OAI) – Ceramic Processing, Characterization

SiC Ceramics Reinforced by SiC fibers (SiC/SiC CMC) are now being developed by NASA, AF, and Industry for Higher-Temperature and Lighter-Weight Engine Components

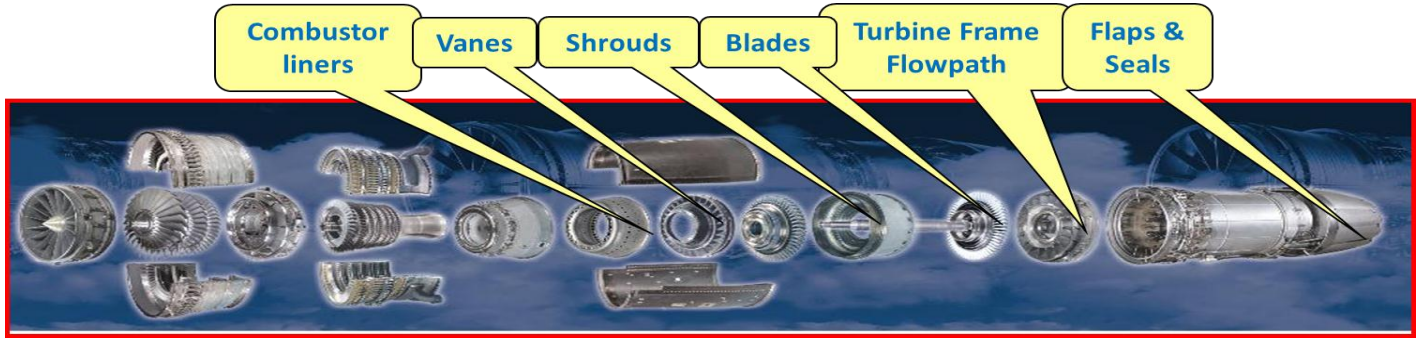


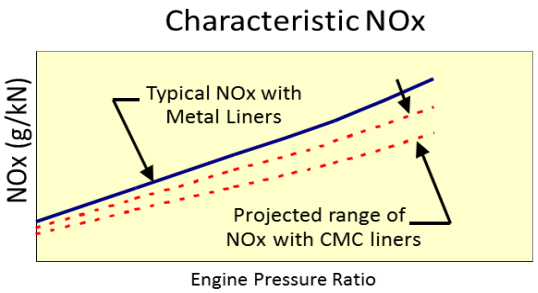


SiC fiber, ~ 10 µm diameter

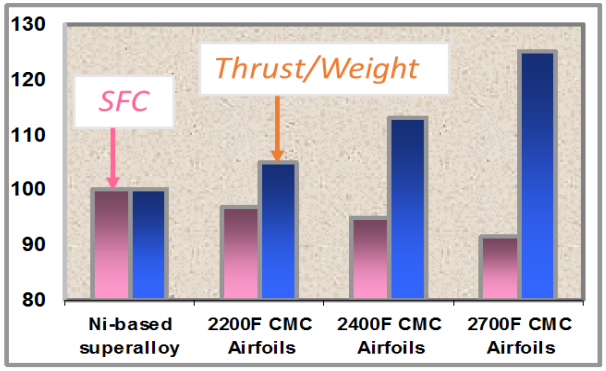
SiC fibers provide damage tolerance by bridging SiC matrix cracks that would otherwise cause catastrophic failure in monolithic ceramics.
***Key CMC Needs*: <u>High strength and creep-resistant SiC fibers at CMC component use temperature</u> and <u>thin weak surface coatings on fibers</u> to allow matrix cracks to deflect around fibers and not through them.**

Current NASA and Industry (GE) Vision for SiC/SiC CMC Turbine Component Applications and Benefits





Reduced NOx Emissions



- *Reduced Specific Fuel Consumption*
- *Increased Thrust-To-Weight Ratio*

General Electric is implementing 2400ºF SiC/SiC CMC in Leap Engine in 2016.
Under new NASA Transformational Tools and Technologies (TTT) Program, NASA GRC is currently tasked to develop 2700ºF SiC/SiC for further emissions and fuel savings benefits. This will require a 2700ºF-capable SiC fiber.

*Key SiC Fiber Property Requirements for Structurally Reliable 2700°F (1482°C) SiC/SiC Composites (*ref. 1*)*

- **Polymer-derived, Polycrystalline, and Small Diameter (10-15 um) for forming capability into complex shapes and lowest fabrication cost.**
- **Near-Stoichiometric Composition (C/Si <1.05) for highest environmental resistance and thermal conductivity.**
- **Tensile Strength > 2000 MPa, which requires as-produced microstructures with pores, flaws, and grains < 500 nm in size.**
- **Large Grains for Highest Thermal Conductivity and Creep Resistance**
  Not only does fiber creep result in time-dependent CMC strains that can become large enough to exceed component displacement allowables, but also results in the growth of cavitation flaws at grain triple points that eventually become larger than 500 nm, thereby reducing fiber strength and possibly causing fiber and CMC rupture during component service. Requires impurity-free microstructures (little if any O, B, Fe, Al) and large as-produced grain sizes up to ~500 nm that (1) reduce the rate of creep and flaw growth and (2) are uniformly distributed across fiber diameter for maximum performance

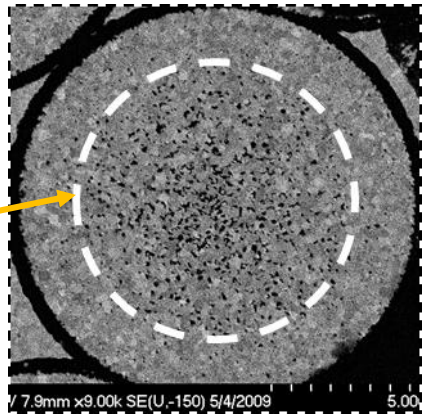
Sylramic-iBN Fibers: Current State-of-the-art SiC Fibers for High Temperature CMC Applications

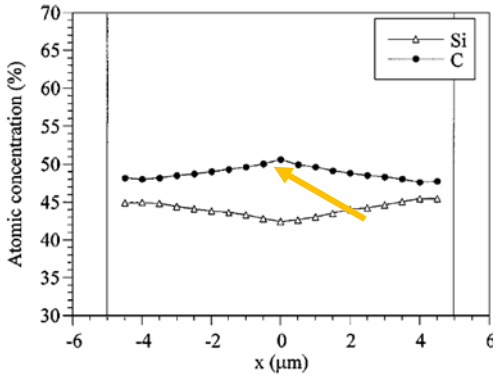
- These fibers are currently derived from the commercial Sylramic™ fiber that was originally developed Dow-Corning. Fabrication of the high-performance Sylramic fibers begins with low-performance oxygen-containing Lox-M SiC fibers from Japan, which are then thermally enhanced by decomposing oxygen out of its microstructure, infiltrating the resulting porosity with boron-containing gas, and then using the boron as a sintering aide to remove the pores and densify the fiber. (ref. 2)
- From subsequent studies at NASA Glenn, high-temperature nitrogen treatments were developed that can remove detrimental boron from the Sylramic fiber (or any other boron-containing SiC fiber), thereby significantly increasing the fiber creep resistance and temperature capability. Treatments also form a thin in-situ grown BN (iBN) layer on each fiber surface, which beneficently acts to separate fibers, provides each fiber with environmental protection, and deflects matrix cracks. (ref. 3)
- For the commercial Sylramic fiber, these patented NASA treatments result in fibers called Sylramic-iBN SiC fibers, but these current SOA SiC fibers only have thermo-structural capability to ~2500°F.

Key Issue with Sylramic-iBN Fibers for 2700ºF Structural CMC Applications

- **Although the Sylramic-iBN SiC fibers contain desirably large grains, they are only located near the surface. In the fiber core, there typically are small grains, pores, and excess carbon that inhibit this region from displaying optimum creep resistance and thermal conductivity, thus limiting CMC thermo-structural capability to ~2500ºF.**

Non-Load Bearing Core Region





Higher Carbon in Core Region

- **Thus a key objective of this Seedling task is to demonstrate UHT fibers with the same or larger grains on the fiber surface as well as throughout the entire fiber microstructure. Fiber creep models developed during Phase II predict that if such a SiC fiber could be developed, it would display creep resistance >20 times greater than the iBN fibers and thus be structurally viable for 2700ºF applications (Pub. 1)**

Other Important Issues with Current Sylramic-iBN Fibers for High-Temperature CMC Applications

(1) <u>High Cost</u>: Compared to the lower-performance oxidation-cured fibers from Japan with a cost ~$1K per kilogram (like the Sylramic precursor Lox-M fiber), commercial Sylramic-iBN SiC fibers cost well over $10K per kilogram related to their multiple high-temperature processes and vendors.

(2) <u>Poor Weave-ability</u>: In contrast to the lower-cost lower-performance SiC fibers, the iBN fibers have a high modulus which limits their capability as multi-fiber tows to be woven without fracture into complex 2D and 3D fiber preforms that NASA and engine end-users need for CMC engine components.

(3) <u>Commercial Availability</u>: Again, in contrast to the lower-cost lower-performance SiC fibers, the Sylramic precursor fibers for the iBN fibers are not currently produced in sufficient volume for engine end-users.

UHT Fiber Task: *Objective and Approach*

OBJECTIVE: Develop and demonstrate UHT SiC fibers in multiple architectural forms, which will eliminate or minimize the four key technical issues currently limiting the SOA Sylramic-iBN SiC fibers for 2700°F CMC components..

APPROACH: Improve the general process steps of the expired Dow Corning patent for the Sylramic fiber (ref. 2) to produce sintered SiC fibers with more uniform microstructures using two types of oxidation-cured commercial SiC fibers, the Japanese-produced "Lox-M" and "Nicalon" SiC fibers. These precursor fibers are not only low cost and commercially available in large volume, but also display low moduli that allows them to be easily woven without fracture into complex-shaped fiber preforms prior to their conversion.

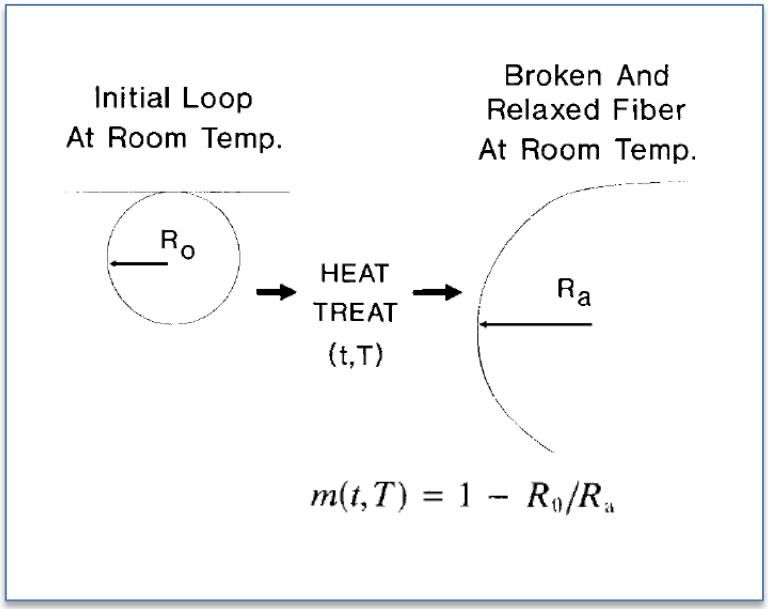
Once improved microstructures are achieved and advanced mechanical properties verified for single sintered fibers, 2D/3D woven preforms of the precursor fibers will be similarly processed and then subjected to the NASA processes for removing the boron from the fibers and producing in-situ grown BN coatings on each fiber.

UHT Fiber: *Experimental Procedure*

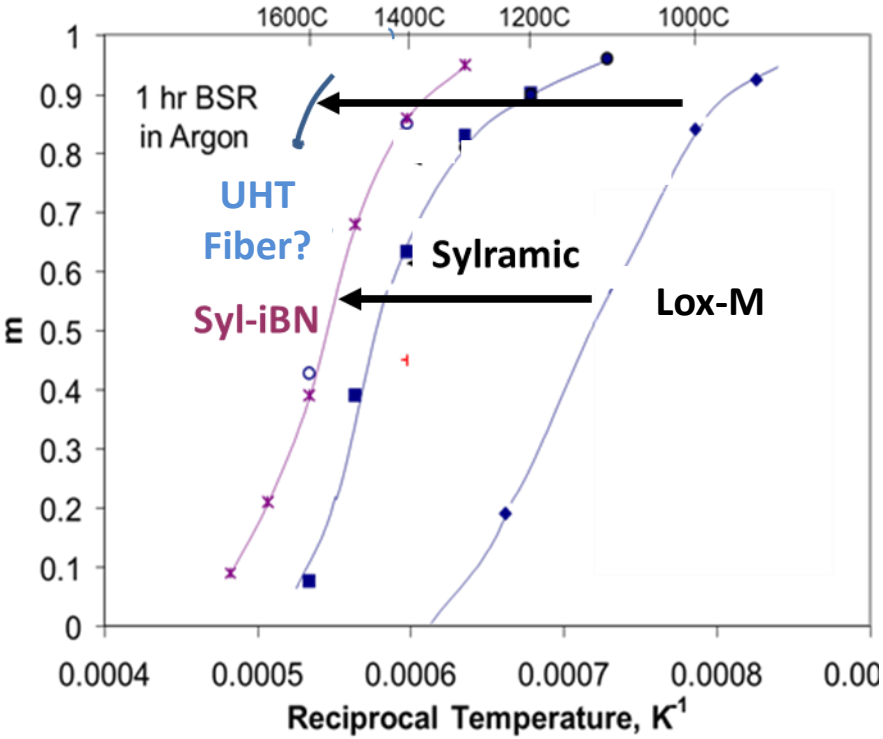
- **For initial process runs, straight multi-fiber tows of commercial Lox-M and Nicalon SiC precursor fibers are placed over a BN boat containing boron-containing powder and processed in a Stage 1 furnace under various time-temperature conditions through the steps of (1) gaseous decomposition of their silicon-oxycarbide phases, (2) doping with boron-containing gas, and (3) pre-sintering at an upper temperature limited by furnace capability.**
- **Processed tows are then removed from the Stage 1 furnace and subjected to final sintering in the Stage 2 one-atmosphere argon furnace at 1800^{o}C for one-hour .**
- **After each process step, microstructures are then characterized for single fibers taken from the tows to monitor and understand the physical-chemical changes occurring in the microstructures.**
- **If the sintered microstructures appear to show no visible pores in the fiber core, the bend creep, tensile strength, and high-temperature rupture-strength of single fibers are measured using GRC-developed procedures and facilities. The results of these tests are then compared against our UHT fiber requirements.**

UHT Fiber: *Fiber Creep Evaluation*

- **For creep and temperature capability evaluation, single fibers are subjected to the NASA-developed Bend Stress Relaxation (BSR) test to evaluate their performance against other SiC fibers.**



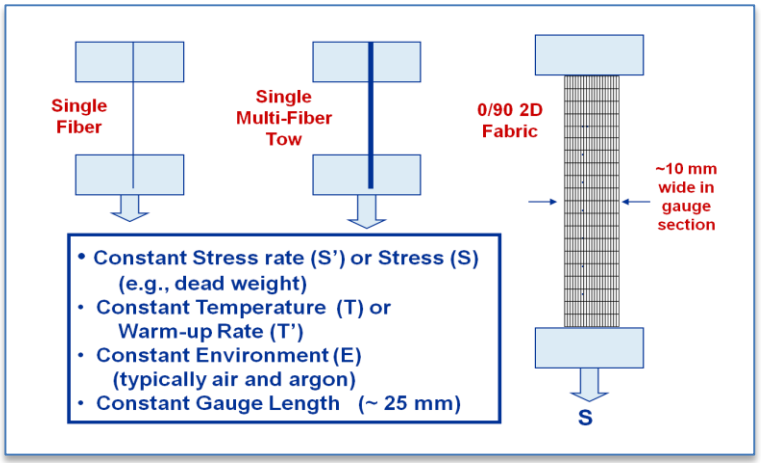
Fiber Bend Tests (Ref.4)



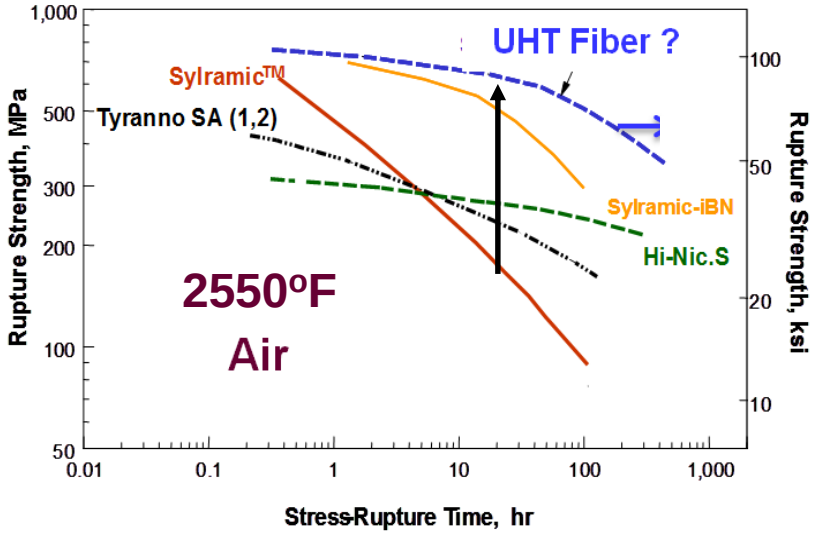
m-ratio Goals for Fiber Development

UHT Fiber: *Tensile Strength Evaluation*

- **When creep-resistant fibers are obtained, the room-temperature tensile strength and high-temperature rupture-strength of the fibers are measured before and after being subjected to NASA's nitrogen processes for the iBN fibers.**



Fiber Tensile Tests (Ref. 5)



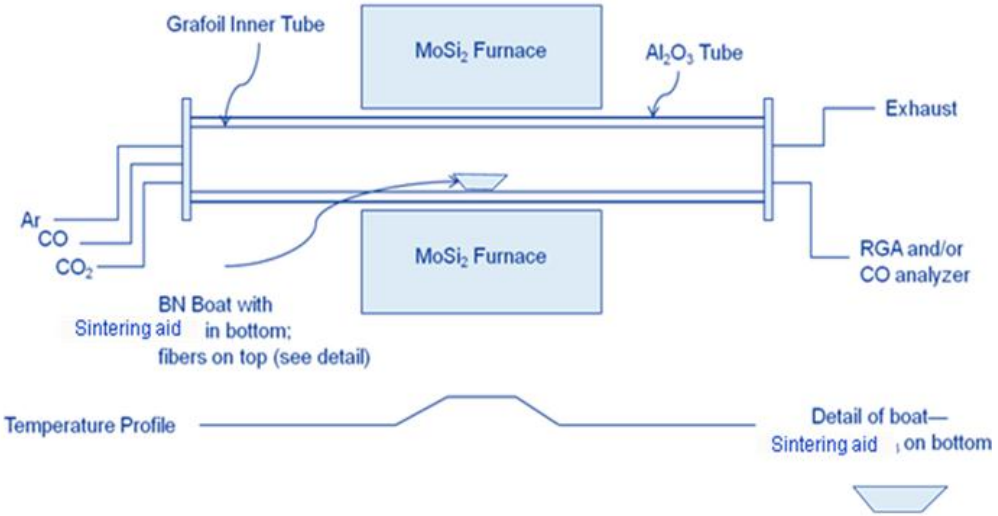
Fiber Rupture Strength Goals

When creep, tensile strength, and rupture strength results are found adequate against the UHT fiber goals, all process and characterization procedures would then be repeated on woven 2D and 3D precursor preforms to understand any concerns with preform conversion.

UHT Fiber: *Stage 1 Facility Development*

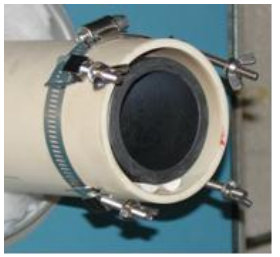
Furnace acquired and up-graded for initial UHT fiber processes

Stage 1 Furnace for Decomposition, Boron Doping, and Pre-Sintering



Small Production Furnace

Graphite tube inside alumina tube with BN spacers



Gas In:
Argon

Gas Out:
Argon
Oxygen
C-O
B-O

UHT Fiber: *Stage 2 Facility Development*

In-house facilities identified for UHT fiber final sintering and iBN processes

Stage 2 Facilities for Sintering and Nitriding

Small, 1 atm.

<u>Gases</u>: Argon, Nitrogen

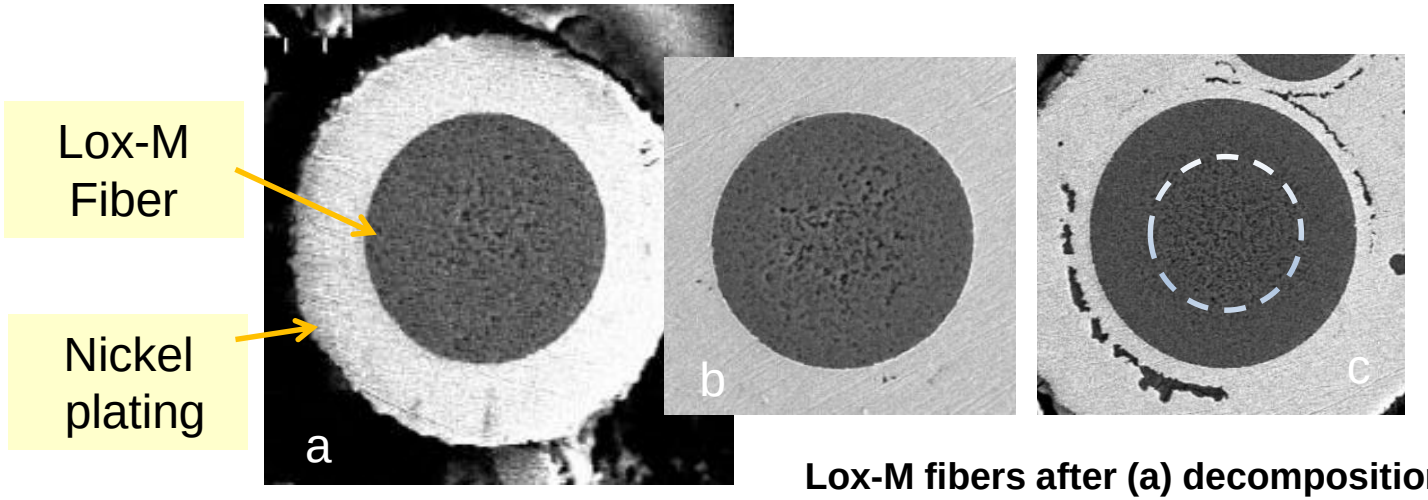
Medium, 1 atm.

Large, high atm.

Large, 1 atm.

UHT Fiber: *Phase I Results: Lox-M Precursor*

Primary precursor fiber focus has been on the Lox-M fiber since it is also the source of the Sylramic and SOA Sylramic-iBN SiC fibers



Lox-M fibers after (a) decomposition, (b) doping, and (c) sintering at 1800°C

<u>Phase I Lox-M Conclusions</u>: Multiple trial runs showed that core pores in sintered Lox-M precursor fiber originate during decomposition and remain after doping and sintering. Possible mechanisms include a high oxycarbide core content leaving pores too large to be sintered and/or residual carbon in the core, which is known as a sintering inhibitor for SiC materials. Thus Phase II efforts centered on a more detailed study of physical and chemical effects occurring during Lox-M decomposition process.

UHT Fiber: *Phase II Results: Lox-M Precursor*

- **At the initiation of Phase II, in order to separate and better understand process effects during the decomposition and doping steps for both precursor types, a manual linear feed-through device was added to the Stage 1 furnace. This allowed movement of the boron-containing boat in and out of the furnace hot zone.**

Device for Better Control of Doping Step

- **Also, it was discovered that when only the decomposition step was performed in the original Stage 1 furnace, boron was deposited on the fibers indicating that boron contamination occurred on the furnace walls in the hot zone area. This issue required the development of a second process furnace dedicated to only the decomposition step without the presence of boron.**

UHT Fiber: *Phase II Results: Lox-M Precursor*

- **To determine the origin of the Lox-M core pores, the new decomposition furnace was used for detailed weight loss studies and physical property measurements on the Lox-M fibers after decomposition at (1360°C). This low temperature was chosen to minimize the agglomeration of any excess carbon in fiber core that occurs during higher temperature decomposition conditions (ref. 6).**

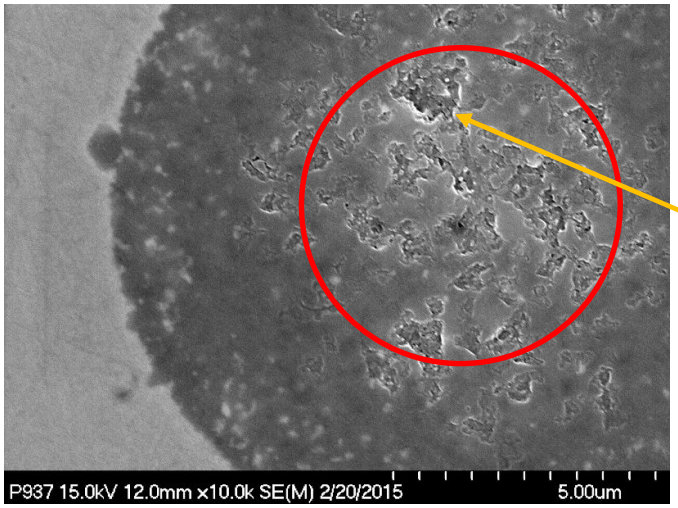
Table 1. Physical measurements after decomposition of the Lox-M precursor fiber at 1360°C

Decomp Hours	Weight Change	Length Change	Diam. Change	Tensile Strength
5	-21.7 %			
12 to 16	-24.7 %	- 3.2%	- ~2 %	~1.1 GPa

- **The weight loss of ~25% for complete decomposition of our current Lox-M fibers indicates an impurity oxygen content of ~13%, which is larger than that indicated in the Dow Corning patent of 11 % for their highest quality Sylramic fibers.**

UHT Fiber: *Lox-M Precursor Status and Future*

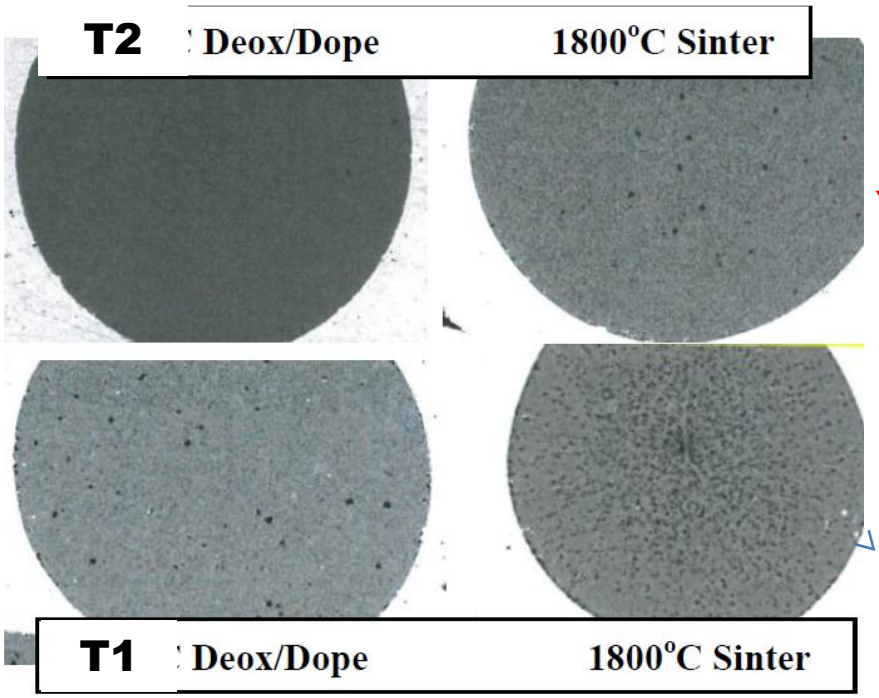
- **Also, after complete decomposition of our Lox-M fibers for 12 or greater hours at 1360°C, microstructures of the decomposed fibers showed exceptionally large pores in the fiber cores.**



Large Core Pores > 500 nm = Low Fiber Tensile Strength

From these observations, it is currently concluded that:
(1) the pores left by decomposition were probably too large to be eliminated during final sintering, an issue that goes back to amount of oxycarbide impurity introduced in original processing of our Lox-M fibers
(2) <u>for our continued Lox-M studies</u>, we will attempt to use Lox-M fibers with lower oxygen and weight loss, which then should be expected to yield smaller and more sinterable core pores.

UHT Fiber: *Phase I Results: Nicalon Precursor*



Process conditions produced:

Uniform Microstructure

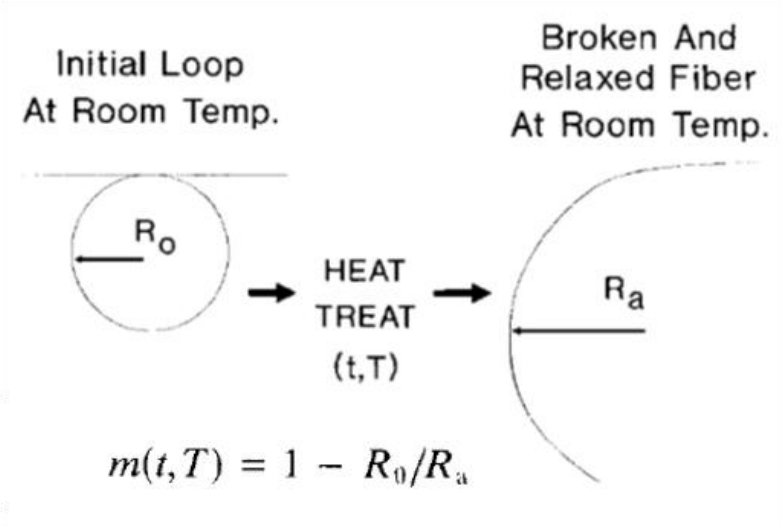
Non-uniform Microstructure

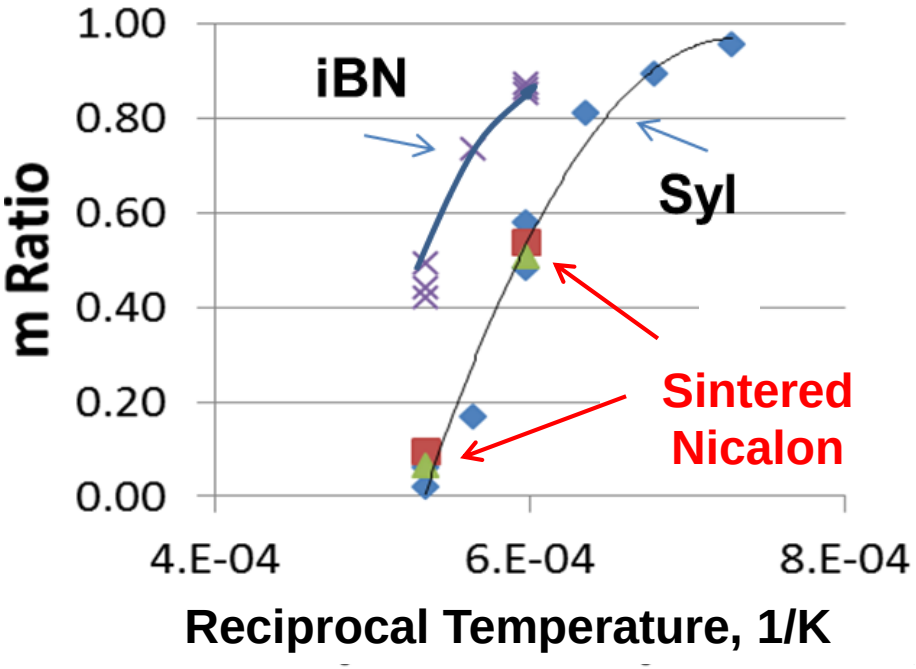
<u>Key Phase I Nicalon Result</u>: Under optimized process conditions, uniform microstructures with <u>no obvious pores</u> were observed after sintering.

Thus in Phase II, those sintered Nicalon fibers with uniform microstructures were subjected to creep , tensile strength, and chemical analyses to check their quality for further processing into a UHT SiC fiber.

UHT Fiber: *Phase II Results: Nicalon Precursor*

- **For creep analysis, the Bend Stress Relaxation (BSR) test was applied to single sintered Nicalon fibers with uniform microstructures.**

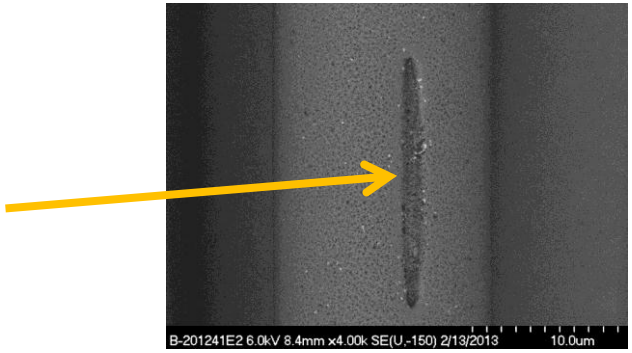




- **BSR creep results show that sintered Nicalon fibers with uniform microstructures display creep behavior equal to that of the Sylramic fibers, indicating GRC processes can produce fibers with equivalent grain structure, which should then be convertible to iBN-types fibers.**

UHT Fiber: *Phase II Results: Nicalon Precursor*

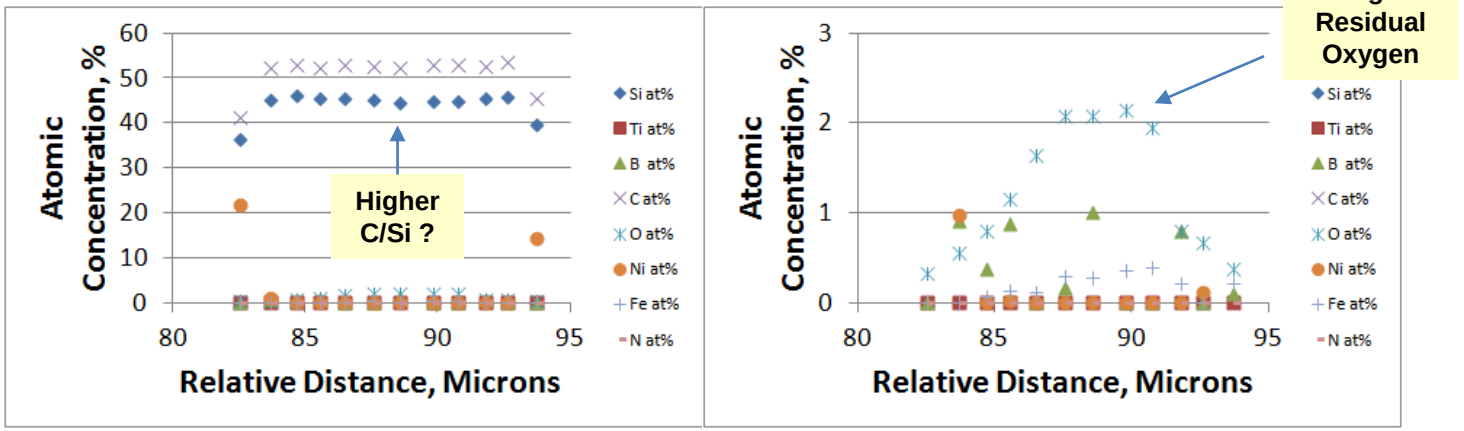
- **<u>For tensile strength analysis</u>, sintered Nicalon fibers with uniform microstructures were tested at room temperature at 1-inch gauge length. Average strengths were found to be lower than those of the commercial Sylramic fibers (~1.5 vs ~3 GPa).**
- **Reduced strength for the sintered Nicalon is currently attributed to tiny kinks along its length as well as surface cracks, which have not been observed in the sintered Lox-M fibers.**



- **One possible mechanism for the kinks and cracks is that as the fiber sintered and contracted in volume, this volume change was non-uniform within the fiber causing local kinking and associated residual stresses that resulted in surface cracking. Trapped oxy-carbide phase in the fiber core may also have resulted in residual stresses.**
- **This kinking issue has been noted in the literature for sintered SiC fibers and has been solved by applying a slight tension to the fibers during any shrinkage process. (ref. 7)**

UHT Fiber: *Phase II Results: Nicalon Precursor*

- **To better understand any chemical sources for the fiber surface cracks, microprobe measurements were made to identify the chemical elements across the sintered Nicalon fiber diameter.**



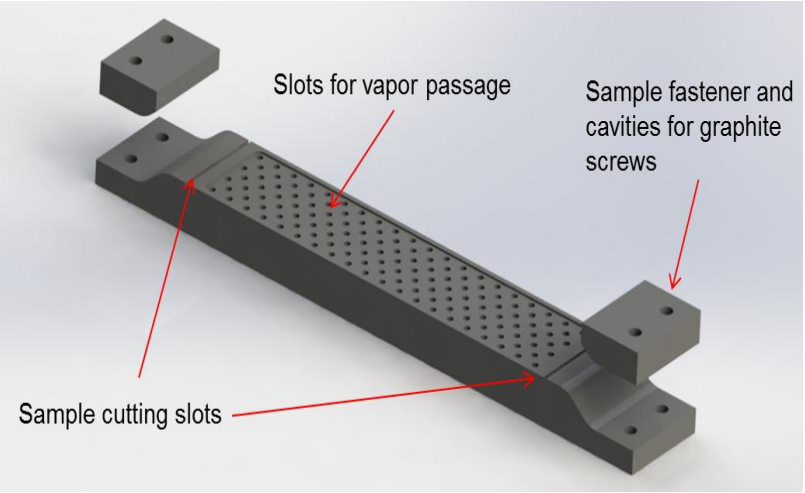
From these observations, it is currently concluded that:

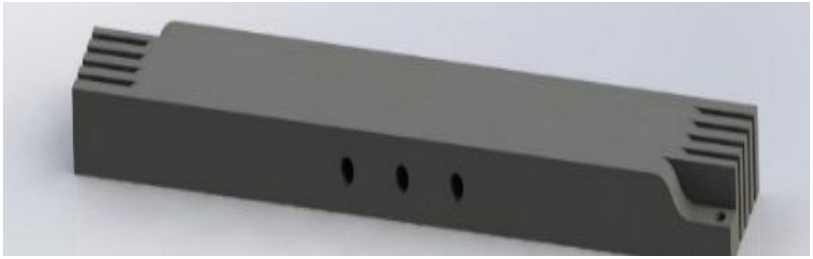
(1) the deox time-temperature conditions for the converted Nicalon fibers, even with apparently uniform microstructures, were not sufficient to completely remove the oxy-carbide phase in the fiber core.

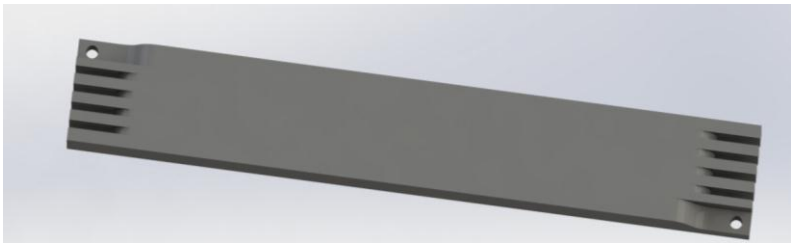
(2) For our continued Nicalon precursor studies, we are seeking improved conditions that result in full decomposition, as well as providing tension on the Nicalon fibers during all process stages.

UHT Fiber: *Phase II Progress: Holders for Fiber Tension*

- **To address the need for tension on the fibers during shrinkage, two new holders for precursor fiber tows have been developed in which the tows are clamped or wound in grooves around a graphite block, which because of its stable size, serves to apply tension to the fibers as they sinter and contract during the high-temperature process steps.**







New Tow Specimen Holders for Applying Tension

UHT Fiber: *Summary of Seedling Accomplishments*

- **Although time consuming, significant progress was made at NASA Glenn in developing the proper process equipment, safety permits, specimen preparation methods, characterization techniques, and property tests for producing and validating a UHT SiC fiber for 2700°F SiC/SiC CMC.**
- **Task efforts verified that the Glenn UHT fiber process methods and facilities can indeed convert the impure microstructures of low-cost highly-available SiC fibers into microstructures equivalent to or better than those of the high-cost low-availability Sylramic SiC fiber. Using NASA's nitrogen processes, these fibers should be directly convertible into fibers with creep behavior similar or better than that of the current SOA Sylramic-iBN fiber.**
- **This result implies that as further studies increase the strength of the converted fibers, processes will be available within NASA and industry for producing fibers similar to the Sylramic-iBN fibers not only within tows, but more importantly within 2D and 3D complex-shaped preforms of CMC components, an important technical result not available today.**
- **Although complete success has not yet been achieved in completely eliminating issues in the converted fiber cores, lessons were learned, and feasible approaches for eliminating these issues will be studied under the TTT program in order to better meet its 2700°F CMC goal.**

UHT Fiber: *Publications and References*

SEEDLING RELATED NASA PUBLICATION

1. J.A. DiCarlo: ***Modeling Creep of SiC Fibers and Its Effects on High temperature SiC/SiC CMC***. Proceedings of 38th Annual Conference on Composites, Materials, and Structures, January 2014, Cape Canaveral, Florida.

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